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13. ABSTRACT (Maximum 200 Words)
Fund from the DURIP award was used to purchase an Atomic Force Microscope (Autoprobe CP from Vecco, CA). The unique closed-loop controller enables the instrument to have precise control of the locations of the AFM tips over a substrate. Such a capability has enabled the local chemical modification of nanostructures directly under the AFM tips. Over the project period, the instrument was purchased and installed and local chemical modification of GaN nanowires have been demonstrated. The transport properties of the nanoscale electronic device made of GaN nanowires between two metal electrodes showed significant change upon the AFM based chemical modification. The effect of applied voltage, reaction time and relative humidity was also studied.

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Final Performance Report (AFOSR #F49620-02-1-0206)

Grant Title: Fabrication and Modification of Metal and Semiconductor Nanostructures Using Atomic Force Microscope

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Final Report: Fabrication and Modification of Metal and Semiconductor Nanostructures Using Atomic Force Microscope

1. Objectives:

1) Purchase and install an atomic force microscope (AFM) with closed-loop controller for precise control of the tip locations;
2) Chemically modify small sections of existing nanowire structures using DPN technique. DPN technique provides a unique capability to deliver chemicals to specific locations on a substrate. It provides an ideal tool to chemically modify a small section of a nanostructures to create nanoscale junctions at specific locations.

2. Status of Effort:

Fund from the DURIP award was used to purchase an Atomic Force Microscope (Autoprobe CP, Vecco, CA). The unique closed-loop feature enable the instrument to have precise control of the locations of the AFM tips over a substrate. Such a capability has enabled the local chemical modification of nanostructures directly under the AFM tips. Over the project period, the instrument was purchased and installed and local chemical modification of GaN nanowires have been performed. The transport properties of the nanoscale electronic device made of GaN nanowires between two metal electrodes showed significant change upon the AFM based chemical modification. The effect of applied voltage, reaction time and relative humidity was also studied.A talk will be given at the 2003 ACS national meeting in September in New York. A manuscript was submitted to JACS.

3. Accomplishments/New findings:

Local Chemical Modification of GaN Nanowires using Electrochemical Dip-Pen Nanolithography:

We have developed a new method for site-specific, Atomic Force Microscope (AFM) fabrication of nanowire heterostructures using Electrochemical Dip-Pen Nanolithography (E-DPN). Specifically, we have created GaN nanowire heterostructures by a local electrochemical reaction between the nanowire and a tip-applied KOH "ink" to produce gallium nitride/gallium oxide heterostructures. By controlling the ambient humidity, reaction voltage, and reaction time, good control over the modification geometry is obtained. Furthermore, after selective chemical etching of gallium oxide, unique diameter-modulated nanowire structures · can be produced. Finally, we have demonstrated the device fabrication applications of this technique by performing in-situ modification of GaN nanowire devices and electronic transport measurements. These results demonstrate that small modifications of nanowire devices can lead to large changes in the nanowire electronic transport properties.

Figure 1 shows a schematic of the E-DPN process. To perform the E-DPN experiment, a KOH "ink" solution is applied to a doped silicon tapping mode AFM tip. The tip is then engaged into feedback and located on a CVD-grown GaN nanowire at a reduced feedback setpoint. A negative bias voltage is applied between the tip and the surface to facilitate an electrochemical reaction between the GaN nanowire and the KOH ink. This reaction forms a gallium oxide heterostructure on the nanowire. The reaction between GaN and KOH has been demonstrated elsewhere in bulk electrochemical etching experiments.[1] After modification, the resulting heterostructure can be characterized by AFM imaging at the original setpoint and bias voltage. This AFM-based modification and characterization scheme is well suited for structure-function studies of nanowire superlattice structures; the
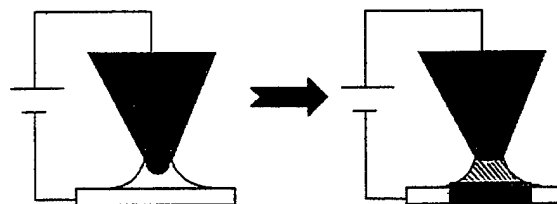

Figure 1. Schematic of the E-DPN modification of GaN nanowires. The AFM tip is first coated with KOH "ink" (blue) and engaged with the nanowire (yellow). During modification of the nanowire, KOH diffuses from the tip to the nanowire surface and electrochemically reacts with the nanowire to produce a gallium oxide heterostructure (green).

transport properties of the wire can be measured, then it can be modified, imaged, and measured again, enabling direct comparisons between nanowire structures and determination of the relationship between nanowire morphology and electronic properties.

Figure 2. Representative AFM surface images of a GaN/gallium oxide heterostructure a) before and b) after selective etching in 1M HCl. The modification in (a) was performed at 40% humidity, 10 V surface-tip bias voltage, 30 sec dwell time. The modification in (b) was performed at 50% humidity, 10V surface-tip bias, 10 sec dwell time.
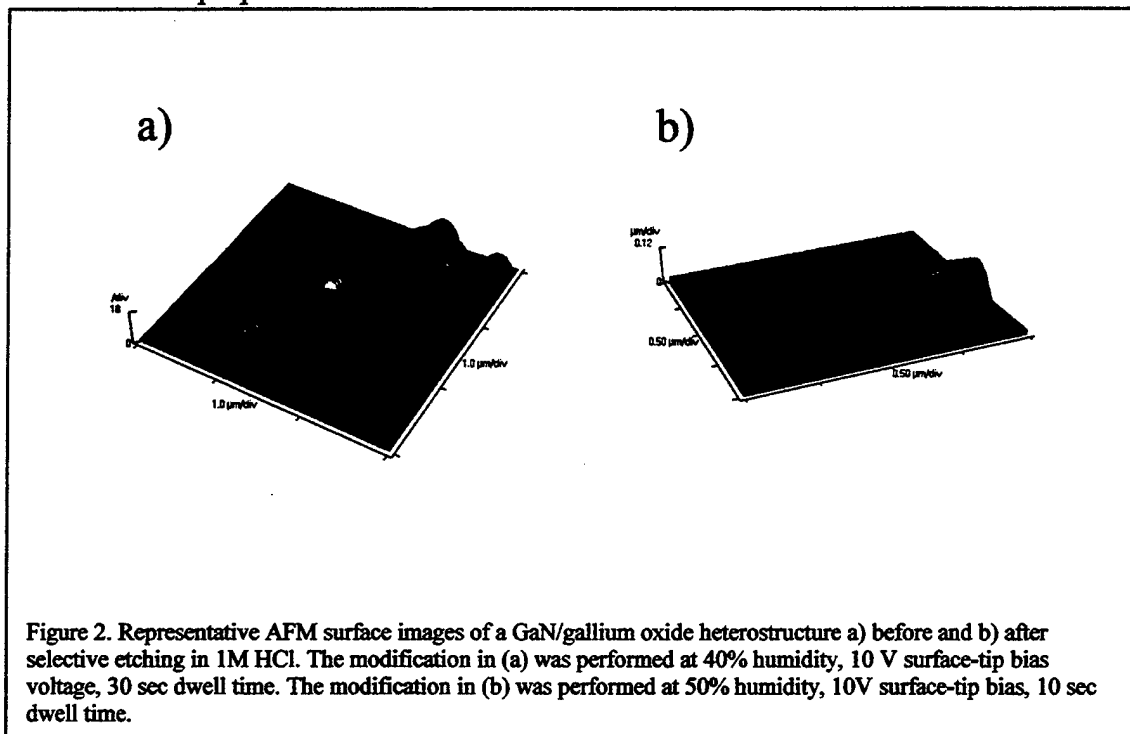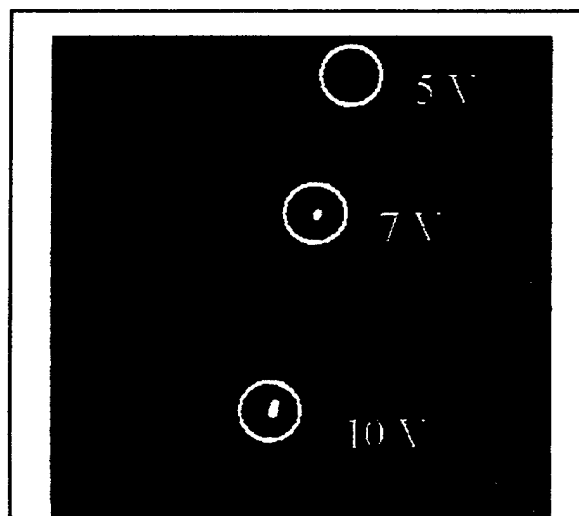
Figure 2a shows a nanowire after E-DPN modification. Gallium oxide has a larger molecular volume than GaN, so the newly formed heterostructures appear as "bumps" along the nanorod. In order to assess how much of the subsurface GaN has been oxidized, the gallium oxide can be removed by selective etching in 1 M hydrochloric acid. The reduction in nanowire diameter is easily observed and is directly related to the amount of gallium oxide formed during the electrochemical oxidation. Figure 2b shows a representative GaN heterostructure after oxide removal.

After examining the available literature, we believe that E-DPN modification is the only way to create these "pitted" GaN nanowire heterostructures. (Figure 2b) Other methods of producing superlattice structures rely on modulating the growth conditions to produce regions with heterogeneous chemical composition. However, due to the vapor-liquid-solid[2, 3] or epitaxial growth[4] mechanisms that are employed, the nanowire diameter is relatively constant. Here we demonstrate the ability to produce novel nanowire structures by modulating its size, rather than its chemical composition. As will be discussed below, this size modulation can lead to interesting electronic properties.

As with other E-DPN processes, the mechanism of surface modification involves diffusion of the ink molecules away from the AFM tip and their electrochemical reaction at the surface. In this case, the tip-applied KOH dissolves in the condensed water meniscus at the AFM tip-surface interface, diffuses to the nanowire and reacts by an electric-field induced electrochemical reaction. The conversion of GaN to gallium oxide requires the oxidation of the semiconductor, so the surface is always positively biased with respect to the tip. As mentioned above, E-DPN is accomplished by reducing the feedback setpoint which accomplishes two things: it increases the electric field at the surface by decreasing the average tip-surface separation and it facilitates the diffusion of KOH from the AFM tip. Other authors have noted that in tapping mode, dip-pen nanolithography is more efficient when the tip driving

Figure 3. AFM image demonstrating the voltage dependence of GaN nanowire modification. This nanowire was modified in three different areas using three different voltages, as indicated above. The modification size increases with increasing applied bias voltage. These modifications were performed at 50% humidity, 10 sec dwell time.

force is increased significantly because it creates more intimate tip-surface contact. Our approach is to reduce the tapping amplitude during modification rather than to increase the driving force, but we believe that it accomplishes the same purpose.

The reaction mechanism for the local modification of GaN nanowires may be somewhat similar to AFM anodization of silicon or other semiconductors, where the high electric field at a biased AFM tip facilitates the electrochemical oxidation of the surface and the transport of reactive oxygen species through the surface oxide layer.[5-8] As demonstrated in Figure 3, significantly more modification of the nanowire was observed as the bias voltage was increased, indicating that the modification is probably also an electric-field dependent process. However, E-DPN modification of GaN produces significantly more surface modification (up to tens of nanometers) than typical AFM anodization (usually less than 10 nm resulting oxide). We believe that this difference is due to the presence of the KOH ink, which dramatically increases the modification rate. In typical silicon anodization reactions, reactive oxygen species are generated in situ from the condensed water layer to produce silicon oxide structures. By using the KOH molecular

Figure 4. AFM image of a GaN nanowire locally modified with KOH ink and KCl ink in an adjacent areas, after selective etching of gallium oxide with 1 M HCl. Inset: AFM image of the same area before selective etching. These modifications were performed at 10 V bias, 50% humidity, 10 sec dwell time.

ink, we believe that larger numbers of reactive oxygen species are available and therefore more oxidation is observed. In fact, simple anodization of the GaN nanowire does not produce large oxide features, presumably because the hydroxide concentration is too low to produce a large amount of oxidation. Control experiments using KCl ink, which cannot participate in the oxidation of the nanowire, confirm this to be true. Figure 4 shows a GaN nanowire modified in one location with KOH ink and in another location with KCl ink. Significantly less modification is observed in the KCl treated area. This observation, coupled with the fact that it is possible to convert relatively large amounts of GaN to gallium oxide, suggests that the KOH ink plays an integral role in this chemical transformation.

The importance of the KOH ink was further demonstrated by assessing the effect of ambient humidity on the modification morphology. Larger areas are modified at higher ambient humidity. This is due to diffusive transport of the KOH ink away from the AFM tip through the condensed water meniscus at the tip-surface interface. As the ambient humidity increases, the spatial extent of the water meniscus also increases, which enables the KOH ink to diffuse further from the AFM tip before reacting with the nanowire. Essentially, the ambient humidity determines the size of the electrochemical "reaction zone" between the AFM tip and the nanowire. This type of humidity dependence and characteristic diffusion based ink dynamics have been observed in other dip-pen nanolithography experiments.[9-11] The observation of a distinct humidity effect on the modification morphology is further evidence of the integral role of KOH transport in heterostructure formation. By controlling the voltage, modification time, and the ambient humidity, the specific morphology of the heterostructure also should be controllable.

We have fabricated a GaN/gallium oxide superlattice structure and studied the changes in its electronic transport properties after each modification step. This device was modified in 2 locations to produce a superlattice structure. Before the first modification, a current vs. voltage sweep (I-V curve) and gate voltage sweep were taken. The nanowire was then imaged and modified using a KOH-coated AFM tip, and I-V and gate measurements were obtained. The wire was etched in 1M HCl for 1 minute to remove the gallium oxide, and I-V and gate measurements were taken again. The device was then modified a second time to create a superlattice structure. The current vs. voltage plots for each modification step are shown in Figure 5a and the gate voltage sweeps are shown in Figure 5b. As demonstrated in these figures, dramatic changes in the electronic transport properties were observed after chemical modification and etching. For this device, fabrication of a GaN/gallium oxide heterostructure resulted in a dramatic decrease in the conductivity of the device and introduced a significant nonlinearity to the I-V curve. We believe that these observations are due to the introduction of a significant electronic transport barrier, such as a tunneling barrier, into the nanowire. After this first modification, the conductance of the nanowire shows a relatively strong gate voltage dependence that was not observed before modification. Interestingly, this gate voltage dependence disappears after chemical etching of
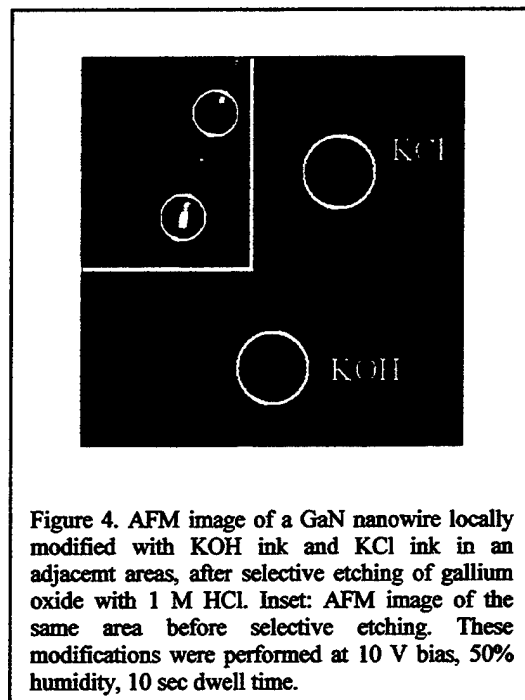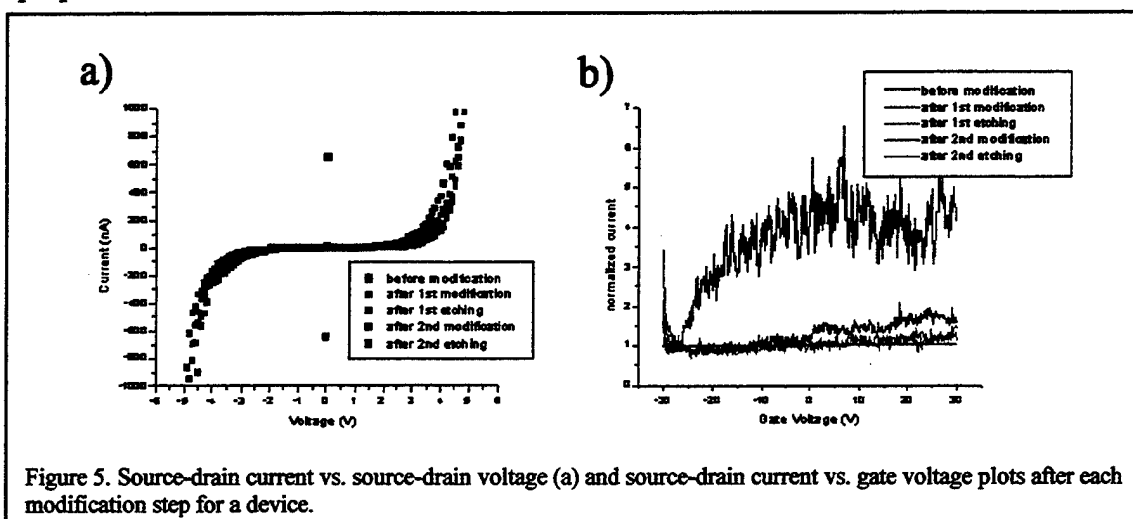
the gallium oxide, indicating that the presence of the gallium oxide heterostructure strongly influences the electronic properties of the nanowire. As mentioned above, after the first modification, another smaller

Figure 5. Source-drain current vs. source-drain voltage (a) and source-drain current vs. gate voltage plots after each modification step for a device.

modification was introduced to the nanowire. This modification did not greatly change the I-V and gate curves, indicating that the first modification dictates the transport properties of this device. This observation makes intuitive sense because the second modification is spatially smaller than the first modification.

The behavior of these GaN devices after modification is very complex and depends greatly on the dimensions of the original nanowire and the extent of modification. We believe that the properties of these devices strongly depend on the nature of the transport barriers, surface defect sites, GaN/gallium oxide band structure interactions, and other effects. We are currently studying these devices to determine the exact nature of the transport phenomena and hope to exploit these behaviors to create devices with useful electronic properties.

In conclusion, we have developed an AFM-lithography based methodology for fabrication of GaN/gallium oxide heterostructures and size modulated GaN nanowires and for in-situ modification of GaN nanowire devices. This technique uses E-DPN to chemically oxidize prefabricated GaN nanowires via a reaction with tip-applied KOH "ink." Furthermore, we have demonstrated that these unique heterostructures possess radically different electronic properties than the original GaN nanowires because the modification creates electronic transport barriers. Using this AFM-based methodology, it is easy to create many types of structures, including single-barrier and superlattice heterostructures simply my moving an ink-coated AFM tip to a desired location and modifying the nanowire by reducing the feedback setpoint and applying an appropriate bias voltage for a desired length of time. In addition to the modification of GaN, this modification scheme may work for other semiconductor nanowires such as CdS or InP. By using other AFM modification techniques and chemistries, we believe that the idea of AFM modification of nanostructures can readily be extended to other systems, including metallic nanowires, carbon nanotubes, or intercalation compounds.

4. Publications:

1. Site-Specific Fabrication of Nanorod Heterostructures: Local Chemical Modification of GaN Nanowires using Electrochemical Dip-Pen Nanolithography, Benjamin W. Maynor, Jianye Li, Chenguang Lu, and Jie Liu, **JACS,** Submitted (2003).

5. Interaction/Transitions:

a. Poster presentations:

Site-Specific Fabrication of Nanorod Heterostructures: Local Chemical Modification of GaN Nanowires using Electrochemical Dip-Pen Nanolithography, Benjamin W. Maynor, Jianye Li, Chenguang Lu, and Jie Liu, ACS national meeting, New York, NY, September 2003.

b. Consulting: N/A
c. Transitions: N/A

6. New Discoveries, Inventions or Patent disclosures:

    None

7. Honors/Awards:

    N/A

8. Reference

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